STRUCTURAL, OPTICAL, ELECTRICAL AND PHOTOCONDUCTING PROPERTIES OF CdSe AND $CdS_X Se_{1-X}$ FILMS PREPARED BY SPRAY PYROLYSIS

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ABSTRACT

The present thesis is devoted to the preparation of thin films of CdSe and CdS_xSe_{1-x} $(0 \leq x \leq 1)$ by spray pyrolysis and a study of the structural, electrical, optical and photoconducting properties of these films. The spray pyrolysis technique is an inexpensive and technically attractive one and has successfully been used to prepare thin films of CdS, $Zn_xCd_{1-x}S$, ZnSe, ZnS and PbS. The purpose of this investigation is to establish the feasibility of this technique to produce good quality CdSe and CdS_xSe_{1-x} films and to study their physical properties.

CdSe and CdS_xSe_{1-x} films have been prepared by pyrolytic decomposition of suitable solutions i.e. aqueous solutions of selenourea (NH_2CSeNH_2) and Cadmium Chloride ($CdCl_2.5H_2O$) for CdSe. Aqueous solution of thiourea (NH_2CSNH_2) was added to this solution for CdS_xSe_{1-x} films. The above solutions were mixed thoroughly and sprayed onto heated glass substrates. The optimum prepratory parameters i.e. substrate temperature, spray rate, ratio of starting solutions etc. were established, for obtaining films with good crystallinity and photosensitivity. X-ray diffraction and electron micrography techniques have been applied to

investigate the crystalline nature and orientation of the films. The transmission and reflection measurements were done on Pye-unicam SP 8-100 spectrophotometer. Indium contacts were made by vacuum evaporation for electrical and photoconductivity measurements. Decay of photo-current was studied to determine the life time of carriers. A variable speed chopper was used to chop the illumination at regular intervals. A storage oscilloscope was used to photograph the resulting curves. Effect of incident illumination, chopping frequency and bias voltage on decay time was studied.

CdSe Films : The films were prepared at different substrate temperatures from 220°C to 400°C. All the films were polycrystalline in nature. The X-ray diffraction patterns revealed that the films deposited at 350°C had the best crystallinity. The reflections from (10,1) planes were most prominent. Films with different ratios of starting solutions were prepared at 350°C. The spray rate was kept at 15 ml/min.

The absorption edge energy (1.7 eV) found from transmission spectra agreed well with the band gap energy of the single crystal CdSe. The edge was sharper for films prepared with one part selenourea and one part $CdCl_2.5H_2O$ (1C1S), which showed that the crystallinity was better in that case. The optical edge was also determined by plotting $(\alpha h\nu)^2$ against $h\nu$. The plot was a straight line implying direct allowed transition.

As grown films had low dark resistance (10^5 ohm) and a photoconductivity gain of the order of 30. The resistance as well as the photosensitivity increased appreciably when the films were annealed in air. This change has been attributed to chemisorption of oxygen. After annealing the films in air at 350°C for 15 minutes, 1C1S films showed best photosensitivity; the gain (dark resistance/light resistance) being as high as 10^5. The plot of dark current vs. ($\frac{1}{T}$) exhibited a valley near room temperature, which has been attributed to the thermal quenching of the sensitization centers. In the dark, all the films exhibit linear I-V characteristics while at high illumination levels, these became superlinear. The photocurrent varies superlinearly with illumination at high illumination levels. The spectral response curve of the resistance showed a dip at 690-700 nm which corresponds to the optical absorption edge. The effect of copper, doping on crystallinity and photosensitivity has been investigated. Thermoelectric power measurements were done to determine carrier concentration. The values obtained were $\sim 10^{16}/cm^3$ for annealed CdSe films.

The carrier mobility had a value ranging from .01 to 0.1 cm^2/V sec. Rise and decay times of photocurrent were studied. The decay time for a typical CdSe films was 1.6 m sec. under 10 m W/cm^2 illumination. The life time increased with increase in illumination level, which gives a clue to the superlinearity shown by the lux-amp characteristics of these films. At 5 mW/cm^2 the life time was 0.8 ms and at 10 mW/cm^2 it was 1.6 ms. Existance of sensitizing centres has been attributed to explain these phenomenon. Thermal quenching experiments determined an hole ionization energy of $\sim$ 0.6eV in these films. The ratio of capture cross-sections (S_p/S_n) was found to be $\sim 10^8$. The high value of (S_p / S_n) suggests that the sensistizing centres are doubly negative. Background illumination was used to determine the life time of majority carriers.

Complete solid solutions of CdS_xSe_{1-x} were formed over the entire composition range. The composition of the films was found out by comparing the results on band gap variation with composition for bulk material. The films were slightly rich in selenium (5-10%). The formula developed by Short et al was used to determine the hexagonal fraction in the structure of the films. All the films had predominently hexagonal structure. No preferred orientation seemed to exist. The lattice parameters a_o, c_o varied linearly with composition and followed Vegard's law. The band gap varied slightly non-linearly with composition, the non-linearity arising due to the excess Se in the films. The spectral response curves of the films showed a dip at wavelengths corresponding to the band gap of the material. The absorption edge shifted continuously with the composition. The decay time was maximum (10 ms) in the case of CdS (x=1) films. This is because of the higher hole ionization energy i.e. 1.0eV, in these films. The value of hole ionization energy changed abruptly at x=0.7-0.8 from CdSe like to CdS like.

PUBLICATIONS

1. Structural, Optical and Photoconducting Properties of Sprayed CdSe films, Thin Solid Films 91 (1982), 55-64.

2. Sprayed CdS_xSe_{1-x} Thin Films, J. Phys. C. Solid State Phys. 15 (1982), 4933-4937.

3. Structural, Electrical and Optical Properties of CdS_xSe_{1-x} Films, Presented in International Conference on Metallurgical Coatings held in San Diego, California, April 18-22, 1983. Thin Solid Films 108, 3 (1983), 313-317.

4. Non Equilibrium Carrier Relaxation in Sprayed CdSe Films, Thin Solid Films 106, 4, (1983),

5. Sensitization Phenomenon in Sprayed CdSe Films, Communicated to Thin Solid Films.

6. Structural and Optical Properties of Sprayed $CuInSe_2$ Films, Thin Solid Films 102 (1983), 291-297 (not included in this thesis).

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